

# Organic Synthesis and Device Testing for Molecular Electronics



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## 1. Introduction

The rapidly developing field of ultra-small electronics is one of the driving forces behind the interest in the synthesis of new molecules as candidates for molecular electronics.<sup>1–8</sup> Molecular electronics is of interest because standard fabrication methods are hitting limits in scaling. We have covered, in other reviews, some of the syntheses of these molecules as well as the large body of work on the theoretical aspects of molecular conduction.<sup>1,9</sup> However, the limitations of the present “top-down” method of producing semiconductor-based devices have been the subject of debate and conjecture since Gordon Moore’s prediction in 1965 that the number of components per integrated circuit would double every 18 months.<sup>10</sup> It was thought that the inherent limitations of the existing technology would lead to a dead end in the next few years with respect to the continued shrinking of circuitry using top-down methods. For instance, silicon’s band structure disappears when silicon layers are just a few atoms thick. Lithographic techniques that are used to produce the circuitry on the silicon wafers are limited by the wavelengths at which they operate. Interestingly, leaders in the semiconductor-

manufacturing world continue to make advances that appear to be pushing “Moore’s Law” beyond its prior perceived limits. Intel<sup>®</sup> has declared that Moore’s Law is here to stay for the next 15–20 years.<sup>11</sup> In the commercial technology of 2004, the copper wires in Intel<sup>®</sup>’s Pentium<sup>®</sup> 4 logic chip being manufactured in their newest 300-mm-wafer fabrication facility in Ireland are 90 nm wide.<sup>12</sup> Strained silicon<sup>13</sup> is but one of several approaches taken by the industry to modify its present silicon-based processes to meet the demands of the development roadmap.

For comparison’s sake, a typical molecule synthesized in our laboratory is calculated to be 0.3 nm wide and 2.5 nm in length.<sup>4</sup> It would take 300 of these molecules, side by side, to span the 90-nm width of a metal line in the most advanced logic chip being made today. The small size of these molecules is emphasized when one considers that 500 g (about one mole) of this wire would contain  $6 \times 10^{23}$  molecules, or more molecules than the number of transistors ever made in the history of the world. This amount of material could be produced using relatively small, 22-L laboratory reaction flasks. Changing the physical characteristics of the molecule is as easy as changing the raw materials used to make it. The small size, the potential of synthesizing huge numbers in small reactors, and the ease of modification of the physical characteristics of the molecules are good reasons for pursuing molecular electronics research. As an example of how far the technology has come, molecular electronics is discussed in the “emerging research devices” section of a recent International Technology Roadmap for Semiconductors,<sup>14,15</sup> and new molecules are a large part of the emerging technology.

We will discuss in the remainder of this review the synthesis and use of discrete molecules, not crystals or films, in molecular electronics devices. The extremely interesting inorganic crystalline nanowires being developed by Lieber and others<sup>16–19</sup> may eventually be used in molecular electronics based circuitry. These nanowires are comprised of crystalline phases and not discrete molecules, and are thus precluded from our definition of molecules for molecular electronics. Most of the work discussed in this review was done in our own laboratories in the past five years. We will first cover the several classes of molecules made

for testing in molecular electronics devices, follow with a short review of molecular electronics test beds,<sup>20</sup> and then discuss in detail two test beds developed in our laboratories.

### 1.1. Oligo(2,5-thiophene ethynylenes) (OTEs)

Oligo(2,5-thiophene ethynylenes) (OTEs) make up one of the first classes of compounds synthesized by our group.<sup>21–24</sup> These rigid-rod, oligomeric molecules, with thioester groups at one or both ends, are made through an iterative divergent–convergent synthesis that allows the rapid assembly of the products, doubling their length at each step. The longest such molecule synthesized is 12.8 nm in length. When deprotected in situ, the thiol groups enable the molecules to adhere to gold (or other metal) surfaces<sup>25</sup> and, therefore, serve as “alligator clips”. When a large number of molecules bond to gold in a regular, packed array through this self-assembly process, the group of molecules is called a self-assembled monolayer (SAM). The bonding of the sulfur atom to gold enables the flow of electricity from the gold metal Fermi levels through the sulfur to the molecular orbitals formed by the conjugated portion of the molecule. The ethynyl units in between the aromatic moieties are used in order to maintain maximum overlap of the orbitals, and to keep the molecules in a rod-like shape. The various side chains appended to the thiophene cores are needed to increase the organic-solvent solubility of the compounds. Unfunctionalized, rigid-rod oligomers of this length suffer from severe solubility problems.

### 1.2. Oligo(1,4-phenylene ethynylenes) (OPEs)

Oligo(1,4-phenylene ethynylenes) (OPEs) form a second class of molecules that has been studied extensively in our laboratory<sup>26</sup> and by others.<sup>27,28</sup> As with OTEs, OPEs can be rapidly synthesized using transition-metal-catalyzed coupling reactions. In this case, the compounds were synthesized in both the solution phase and on a polymer-based solid resin. As with OTEs, C<sub>12</sub> side chains were employed to impart organic-solvent solubility to the products. The use of longer side chains, such as C<sub>14</sub> or longer, can result in side-chain interdigitation, which leads to insolubility problems rather than increasing the solubility.

To further explore the organic functionality necessary for molecules to carry an electric current, we synthesized a group of 2-terminal OPEs that contain interior methylene or ethylene group barriers to electrical conduction, and that could be tested using presently known test beds.<sup>29</sup> Each of these OPEs was synthesized using relatively straightforward chemistry, a fact that illustrates our earlier claim that it is easy to explore molecular wire space by changing just one or two aspects of the synthesis. We also synthesized a series of OPEs with different alligator clips to see what effect that variation would have on the conductance of the molecules.<sup>30</sup> Additionally, we have developed combinatorial chemistry routes that are capable of synthesizing tens to hundreds of new OPEs at a time.<sup>31</sup>

Our group’s “mononitro” OPE<sup>32</sup> is a highly tested compound by many research groups because of its room-temperature, negative-differential-resistance (NDR) behavior.<sup>33</sup> In one synthesis of this OPE (**Scheme 1**), separation of the intermediates by chromatography had limited success; therefore, after a simple workup, each product mixture was used in the next step without further purification. After the deprotection step, purification was greatly simplified and intermediate **1** was isolated pure in 35% yield over 3 steps. The Sonogashira–Castro–Stephens coupling of **1** with **2** provided the mononitro OPE (**3**) in a moderate yield of 47%. The low yield in this last step is presumably due to the acetyl portion of the thioacetate moiety in the coupled product

being susceptible to complexation with the Pd. When this occurs, the catalytic cycle is retarded. The yields of these coupling reactions can generally be increased by using higher percentages of triphenylphosphine as ligand. This observation supports our hypothesis that triphenylphosphine helps to keep the Pd in the catalytic cycle by preventing it from binding to the thioacetate functionality.

An improved synthesis of **3** alleviates the lack of selectivity in the initial coupling step of Scheme 1 by utilizing a monohaloarene coupling partner in each coupling reaction (**Scheme 2**).<sup>32</sup> Moreover, a key to obtaining the higher overall yield of **3** is to use 5 mol % Pd, 10 mol % Cu(I), and 20 mol % PPh<sub>3</sub> (dubbed the “5,10,20” method). A lower amount of PPh<sub>3</sub> (e.g., 12.5 mol %) normally results in much lower coupling yields as mentioned in the preceding paragraph. Although the synthesis depicted in Scheme 2 involves two additional steps as compared to that depicted in Scheme 1, the purification of the intermediates in Scheme 2 is simpler and less time-consuming, and the overall yield of **3** is higher. Moreover, the coupling of **12** with **2** led to the regioisomeric “nitro-up” OPE (**13**) in 73% yield (46% overall yield from **8**). The “5,10,20” catalyst loading method was utilized to synthesize intermediate **12**, a regioisomer of **1**, in 63% yield over four easy steps (**Scheme 3**).<sup>32</sup> A prior route had afforded **12** in only 32% yield over three arduous steps.<sup>32</sup>

The “5,10,20” catalyst loading method also proved its value in the synthesis of the analogue of **3** containing two terminal thiol groups. These thiol groups function as “alligator clips” when contacting two metal surfaces or cross-linking nanoparticles. The bis(thioacetyl) intermediate, **16**, was deprotected with sulfuric acid to give the corresponding bis(thiol) **17** in 77% yield (**Scheme 4**).<sup>32</sup> Compound **17** is desirable, since no in situ deprotection of the thiols is required when assembling the OPE onto metal surfaces or nanoparticles. This makes the assembly process simpler and faster. It is worth noting that the base-promoted deprotection of **16** failed, and that strict exclusion of air from the preparation of **17** is required, even during workup, because aromatic thiols are susceptible to air oxidation.

The synthesis of the unfunctionalized (**21**) and functionalized (**22**) dinitro-bipyridyl OPE derivative is described in **Scheme 5**.<sup>34</sup> Compound **21** was needed for cyclic voltammetry (CV) studies, whereas thioacetate **22** has shown interesting electrical properties in device testing.<sup>35</sup> OPE derivative **22** was found to have single-molecule device properties in a number of test beds, and its stability as a molecular switch is remarkable.<sup>35</sup> While the origin of this stability is still unknown, we are synthesizing several analogues to help pinpoint the salient features needed for stable switching and to further guide our theoretical efforts.

We recently reported the advantages of using the mononitro thiol–thioacetate terminated OPE **23** in the NanoCell, a functioning electronic memory device.<sup>36</sup> We also detailed the synthesis of **23** and the related compounds **24–28** (**Figure 1**).<sup>37</sup> Compounds **23–28** were designed to allow for self-assembly of the molecules via the free thiol<sup>29,38</sup> or nitrogen atom,<sup>39</sup> while protecting the other sulfur atom as a thioacetate to ensure molecular directionality and to inhibit cross-linking if SAM assembly on nanorods is desired. Following initial assembly, the acetate can be removed with NH<sub>4</sub>OH or acid to afford the thiol, which can be assembled onto another metallic material.<sup>40</sup> For mononitro compounds **23**, **27**, and **28**, this process affords a monolayer with all the nitro groups oriented in a common direction. The orthogonal-functionalization approach was thus exploited in the synthesis of **23** (**Scheme 6**),<sup>37</sup> whereby a Boc-protected sulfur atom at one end was deprotected with

trifluoroacetic acid (TFA),<sup>41</sup> leaving the thioacetate moiety on the other end intact.

### 1.3. Oligo(1,4-phenylene vinylenes) (OPVs)

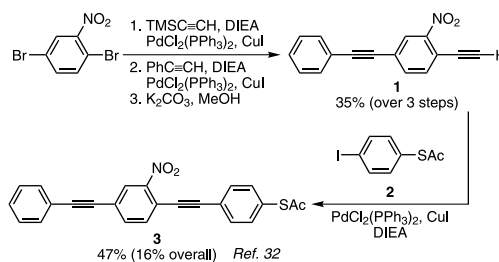
In order to design more efficient molecular devices (lower impedance, larger ON:OFF ratios, and longer electronic hold times), several features of the molecules needed to be optimized. To achieve the highest efficiency in terms of energy used, transport should be maximized across the molecular device. Recent work by Sikes et al. has shown that electrical transport is higher through oligo(phenylene vinylenes) (OPVs) than through OPEs.<sup>42</sup> Similar results, both theoretical and experimental, have been obtained by Kushmerick et al.<sup>43</sup> We have designed syntheses of OPVs using acetyl protecting groups,<sup>34</sup> but found them difficult to complete; therefore, the more robust ethyltrimethylsilyl group was used to protect the thiol. With the completed ethyltrimethylsilyl-protected compounds in hand, initial assembly experiments using in situ deprotection failed to form adequate SAMs. It was subsequently determined that the acetyl precursor was preferred for the in situ deprotection and assembly. The ethyltrimethylsilyl group was thus replaced with the acetyl group using excess TBAF for deprotection, followed by the addition of excess acetyl chloride. This approach afforded the desired acetyl-protected OPVs **37**, **38**, and **39** in moderate-to-high yields (eq **1**).<sup>34</sup> In other work, we have used fluororous-mixture synthesis (FMS) to prepare a library of OPVs via combinatorial methods.<sup>44</sup>

### 1.4. Synthesis of U-Shaped Molecules

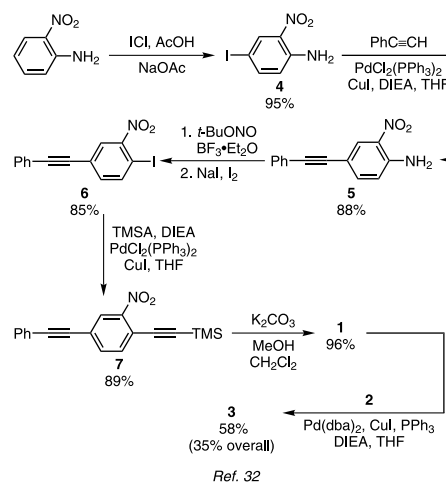
When evaluating an organic molecule for potential application as a molecular device component, the electronic nature of its functional groups as well as its molecular geometry determine, to a great extent, the electronic characteristics of the device. This motivated us to pursue the synthesis of new OPEs with extended conjugation exemplified by a 1,3-bridging aromatic ring linking two linear phenylethynyl backbones.<sup>45</sup> Six new “U-shaped” OPEs were synthesized, based on 3,3’-diethynyl[1,1’;3’,1’]terphenyl and 1,8-diethynylanthracene. We proposed that the analysis of U-shaped molecules would aid in developing a better understanding of the electronic properties of OPEs, when they are present in active molecular electronic devices. Two of the six U-shaped OPEs synthesized have nitro groups as potential redox centers, and all six targets are end-functionalized with acetyl-protected molecular alligator clips, which, upon deprotection, afford the thiolates or thiols for covalent surface attachment. The terphenyl targets have a relatively low rotational barrier and larger dihedral angles at the central terphenyl ring, whereas the anthracene derivatives have a higher rigidity based on the fully conjugated and planar 1,8-diethynylanthracene backbone. The protocol employed in the synthesis of this group of OPEs is illustrated by the preparation of **44** (Scheme 7).<sup>45</sup>

### 1.5. Synthesis of Fluorinated OPEs

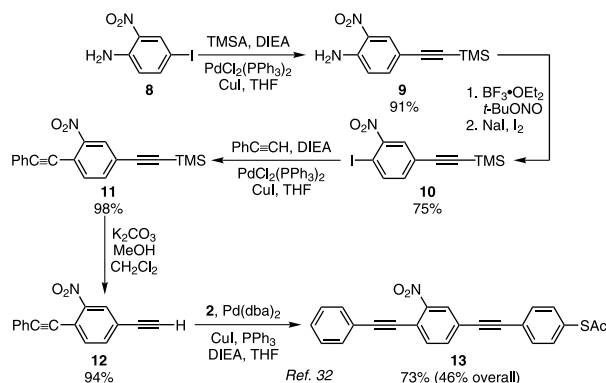
In general, the use of fluorocarbons as organic thin-film precursors produces materials with increased thermal stability and chemical resistance. The corresponding intermolecular attractive forces are less dominant, and thus the molecular interactions at the chemical interface become more pronounced, as compared to the nonfluorinated analogues. This is especially true for aromatic fluorine compounds. These characteristics could be critical for high-temperature processes like gas-phase physical vapor deposition (PVD). With the goal of producing several new molecular electronics candidates that would be appropriate for PVD applications, we synthesized nine oligomers.<sup>46</sup> Although



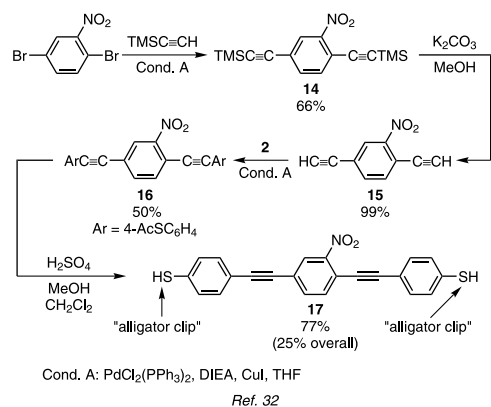
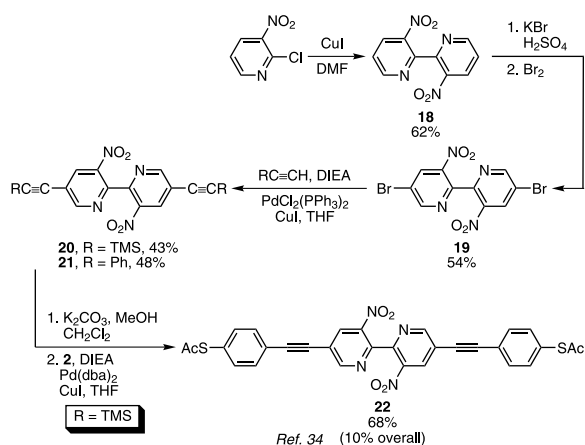
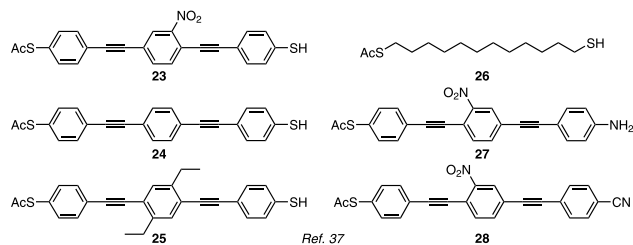
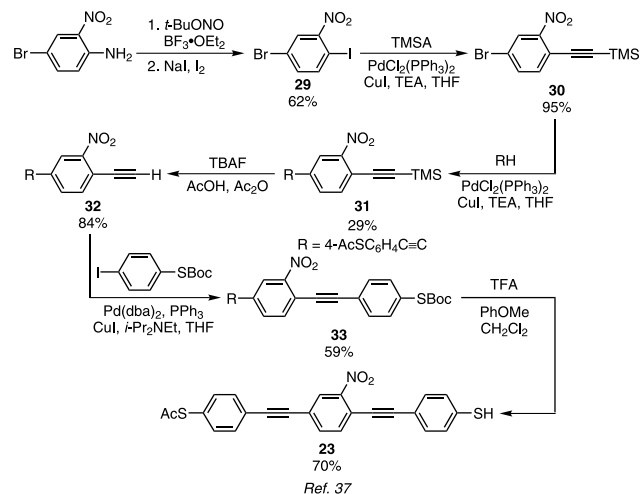
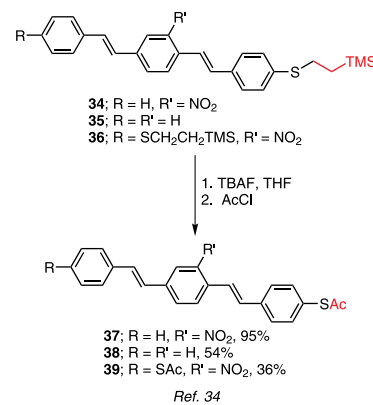
Scheme 1. Synthesis of “Mononitro” OPE **3**.



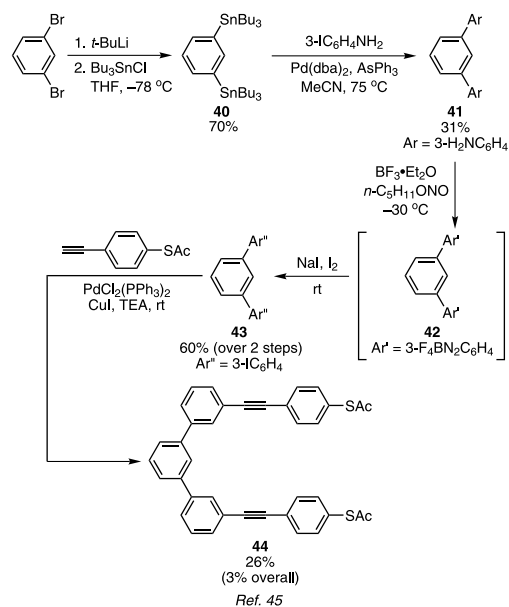
Scheme 2. An Improved Synthesis of “Mononitro” OPE **3**.



Scheme 3. Synthesis of “Nitro-Up” OPE Regioisomer **13**.

**Scheme 4.** Synthesis of OPE **17** Containing Two "Alligator Clips".**Scheme 5.** Synthesis of the Dithioacetate Dinitrothiopyridyl OPE **22**.**Figure 1.** Structures of the Target Compounds **23–28**.**Scheme 6.** The Orthogonal Functionalization Approach in the Synthesis of "Mononitro" OPE **23**.

eq 1

**Scheme 7.** Synthesis of U-Shaped OPE **44**.

most of the synthetic steps gave only moderate yields, their relative simplicity and ease prompted us to use them for the synthesis of several different functionalized cores and alligator clips, as exemplified by the synthesis of OPE **51** (Scheme 8).<sup>46</sup> The core of these oligomers was functionalized with nitro or amino groups, which have been widely reported to act as redox centers for switching effects, and the ends were functionalized with various alligator clips, including free thiols, nitriles, and pyridines for making molecular-scale junctions with several bulk contacts. Each molecule contained an electron-deficient pentafluoro aromatic ring as the dipole moment director.

### 1.6. Synthesis of Oligoanilines

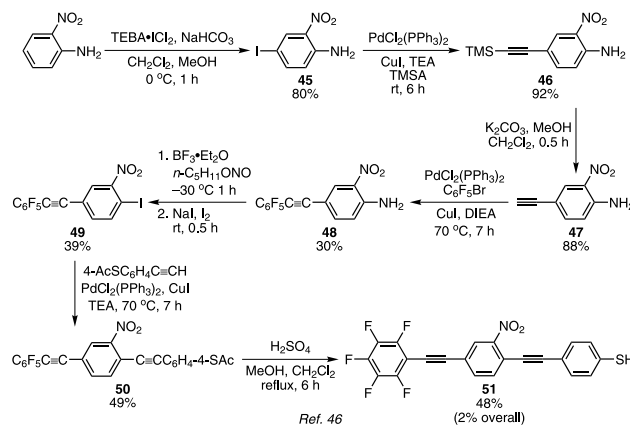
We have designed and synthesized oligoaniline-based molecules as a new class of potential switching and memory-type devices.<sup>47</sup> Oligoanilines offer the possibility of reversibly oxidizing between different conductivity states in a controlled fashion—between the nonconductive leuco base and the conductive emeraldine salt—giving rise to a potential ON:OFF “memory-like” effect. We incorporated the sulfur-based alligator clips into the molecules (e.g., **53**; Scheme 9), and synthesized oligomers with methylated nitrogen atoms to ensure oxidation only to the highly conductive emeraldine salt and not to the nonconductive emeraldine base or leuco salt (provided pH is controlled). Additionally, each nitrogen atom is capable of losing one electron, permitting oligoanilines to offer multiple independent electronic states.

### 1.7. Synthesis of OPE Diazonium Salts

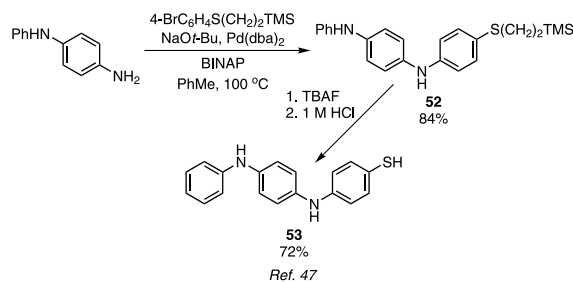
Using arenediazonium salts that are air-stable and easily synthesized, we developed a one-step, room-temperature route to the formation of direct covalent bonds between  $\pi$ -conjugated organic molecules and three material surfaces: Si, GaAs, and Pd.<sup>48</sup> The Si can be in the form of single-crystal Si—including heavily doped p-type Si, intrinsic Si, and heavily doped n-type Si—on Si(111), Si(100), and n-type polycrystalline Si. The formation of the aryl–metal or aryl–semiconductor bonds was confirmed by evidence from ellipsometry, reflectance Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV) and atomic force microscopy (AFM) analyses of the surface-grafted monolayers. This spontaneous diazonium activation reaction offers an attractive route to highly passivating, robust monolayers or multilayers on many surfaces, which allow for strong bonds between surface atoms and carbon in molecular species that are nearly perpendicular to the surface of Si(111).

We have used a similar protocol for the formation of carbon nanotube–molecule–silicon junctions.<sup>49</sup> To our knowledge, this was the first report of a procedure to covalently attach single-walled nanotubes (SWNT) to a silicon surface that does not require a CVD growth process. In addition to functioning as the linker units, OPEs and related conjugated molecules can serve as electronically active moieties in sensor and device embodiments. Hence the union of easily patterned silicon with the often hard-to-affix nanotubes can provide a critical interface methodology for electronic and sensor arrays.

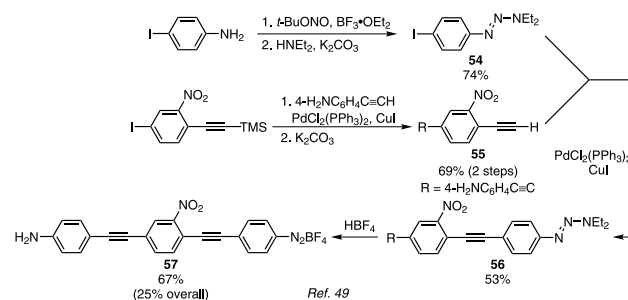
In this work, chemical orthogonality provides chemoselection for both substrate and nanotube attachment, while OPEs provide a rigid structure to minimize molecular looping upon surfaces. The target OPE molecules contain a diazonium salt on one end and an aniline moiety on the other end (e.g., **57**; Scheme 10).<sup>49</sup> This design allows for selective assembly via the first diazonium salt onto a hydride-passivated silicon surface followed by diazotization of the aniline using an alkyl nitrite.



Scheme 8. Synthesis of Fluorinated OPE **51**.



Scheme 9. Synthesis of the Monothiol Oligoaniline **53**.



Scheme 10. Synthesis of Orthogonally Functionalized Diazonium Salt **57**.

Once formed, the new diazonium salt, covalently bound to the Si surface, will react with an aqueous solution of individualized, sodium dodecylsulfate (SDS) wrapped SWNTs (SWNT/SDS)<sup>50</sup> to produce a covalent attachment of the SWNTs to the silicon surface via the OPEs (Scheme 11).<sup>51</sup>

## 2. Molecular Electronics Device Assembly and Testing

In this section of the review, we will present some additional background information on the procedures used in the assembly of molecular electronics devices, and discuss two test bed devices that we have recently developed. A complete discussion of the test beds used in molecular electronics can be found in our recent review.<sup>20</sup>

### 2.1. Self-Assembly of Molecules

In using molecular components to make electronics devices, a problem arises when one attempts to place the molecules in known positions with each end of the molecules connected in a known manner to the circuit. As of the time of this writing, no efficient method besides self-assembly exists for the individual placement of billions of molecules reproducibly in known positions. It is thus easy to understand why so much research has been conducted on self-assembly as it relates to molecular electronics. According to Whitesides,<sup>52</sup> “a self-assembling process is one in which humans are not actively involved, in which atoms, molecules, aggregates of molecules and components arrange themselves into ordered, functioning entities without human intervention.” Whitesides reviewed the principles of molecular self-assembly over a decade ago,<sup>53</sup> including the possibility of using self-assembly to make semiconductor devices.

In our early work to lay the foundation for the use of self-assembly in the construction of electronic devices from molecules, SAMs of various thiol-containing molecules were formed on the surface of gold and analyzed using ellipsometry, XPS, and external reflectance FTIR.<sup>54</sup> It was found that the thiol moieties dominated the adsorption on the gold sites, and the direct interactions of the conjugated  $\pi$  systems with the gold surface were weaker. The tilt angle of the long molecular axis of the thiol-terminated SAM, that was derived from a substituted OPE, was found to be  $\sim 20^\circ$  from the normal to the substrate surface. In situ deacetylation of the thioacetyl group with  $\text{NH}_4\text{OH}$  led to the formation of the SAM without isolation of the oxidatively unstable free thiol.

### 2.2. Devices and Test Beds Made with Molecules

A series of OPEs<sup>26</sup> and OTEs<sup>21</sup> of increasing lengths were synthesized via solution- and solid-phase chemistry, in order to explore the physical and electronic characteristics of the molecules. The working theory was that conductance occurred through the overlapping  $\pi$ -molecular orbitals of OPEs<sup>55,56</sup> and OTEs. Later work has concentrated on OPEs in order to maximize molecular orbital overlap. The thiol-terminated alligator clips that have been used to attach the molecules to metal surfaces form robust bonds to these surfaces ( $\sim 50$  kcal/mole or  $\sim 2$  eV).<sup>57</sup> Theoretical work using density functional theory (DFT) has indicated that the best alligator clip would be sulfur followed by selenium and tellurium; however, a direct aryl-metal bond might be best.<sup>58</sup> Recent work done in air- and ultrahigh-vacuum (UHV) scanning tunneling microscopy (STM) on SAMs formed from S- or Se-terminated terthiophene molecules has shown that, regardless of the tunneling conditions, selenium provides a better coupling link than sulfur.<sup>59</sup>

Along with our colleague Mark Reed, we measured the conductance of a molecular junction in 1997.<sup>60</sup> Two gold wires were covered with SAMs of benzene-1,4-dithiol in THF. The wires were bent until they broke, and the broken ends were brought together in picometer increments via a lateral piezoelectric crystal, until the onset of conductance was measured. The spacing between the tips of the wires was set to about 8.0 Å using calibrated piezo voltage measurements, in agreement with the calculated molecule length of 8.46 Å. That the conductance of a single molecule was measured was supported by the experimental data. The experimental findings were corroborated by a large body of theoretical data on the subject, which has recently been reviewed.<sup>61</sup>

In 1999, large ON:OFF ratios and negative differential resistance (NDR) were measured in molecular electronic devices constructed using functionalized OPEs and a nanopore test bed.<sup>62</sup> The nanopore test bed, shown in Figure 2, was constructed by etching, via electron beam, a small hole 30 to 50 nm in diameter, in a resist-containing silicon nitride ( $\text{Si}_3\text{N}_4$ ) membrane. The conditions of the etch were such that a bowl-shaped geometry was produced, with the hole at the bottom of the bowl. The bowl was then filled with evaporated Au, and the device was placed in a solution of functionalized OPE **58**. After allowing the SAM to form under basic conditions for 48 h, the device was removed from the solution, quickly rinsed, and placed on a liquid-nitrogen cooling stage for the deposition of the bottom Au electrode via evaporation. The device was then diced into individual chips that were bonded onto packaging sockets. The electrical characteristics of the packaged test beds were measured in a variable-temperature cryostat using a semiconductor parameter analyzer.

Figure 3 shows the NDR peak measured in a nanopore test bed device containing a SAM of **58** at 60 K. Note that at about 1.75 V, the SAM became conductive to a peak of 1.03 nA at about 2.1 V. The conductance then sharply dropped to about 1 pA at 2.2 V. The SAM therefore acted as an electrical switch, turning ON then OFF depending on the applied voltage. The peak-to-valley ratio (PVR) was about 1030:1. A SAM of **58** in a two-terminal cell provided electronically programmable and erasable memory with long bit-retention times.<sup>63</sup>

### 2.3. The NanoCell

A NanoCell is a two-dimensional unit of juxtaposed gold electrodes fabricated atop a Si/SiO<sub>2</sub> substrate, (Figure 4, top). A discontinuous gold film is vapor-deposited onto the SiO<sub>2</sub> in the central region (Figure 4, bottom). The NanoCell approach, as previously described and simulated,<sup>1,64</sup> is not dependent on placing molecules or nanosized metallic components in precise orientations or locations. For the most part, the internal portions are disordered, and there is no need to precisely locate any of the switching elements. The nanosized switches are added in abundance between the micron-sized input/output electrodes, and only a small percentage of them need to assemble in an orientation suitable for switching. The result of the NanoCell architecture is that the patterning challenges of the input/output structures become far less exacting, since standard micron-scale lithography can afford the needed address system, and fault tolerance is enormous.<sup>64</sup> However, programming is significantly more challenging than when using ordered ensembles. Remarkably, the NanoCell exhibits reproducible switching behavior with excellent peak-to-valley (PVR) ratios, peak currents in the milliamperere range, and reprogrammable memory states that are stable for more than a week with substantial 0:1 bit level ratios.

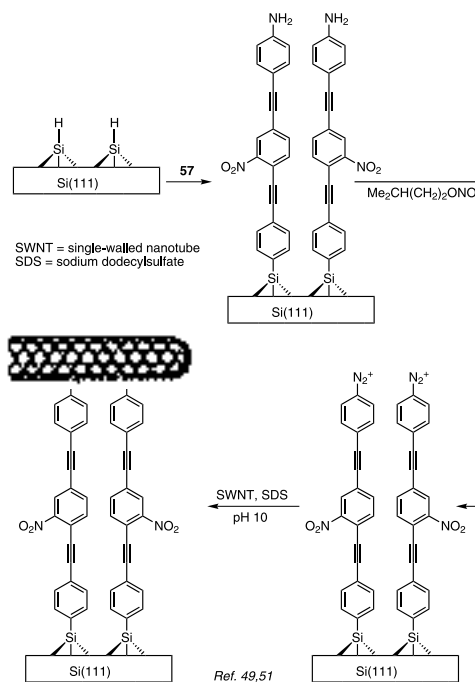
Gold nanowires were added to a vial containing **23** in  $\text{CH}_2\text{Cl}_2$ . The vial was agitated to dissolve the polycarbonate membrane around the nanowires, subsequently forming **23**-encapsulated Au nanowires via chemisorption of the thiols onto the nanowires. Because the thiol groups are far more reactive toward Au than the thioacetyl groups,<sup>54</sup> this procedure leaves the latter projecting away from the nanowire surfaces.  $\text{NH}_4\text{OH}$  and ethanol were added, and the vial was agitated for 10 min to remove the acetyl group. A chip containing 10 NanoCell structures was placed in the vial, and the vial was further agitated for 27 h to permit the nanowires to interlink the discontinuous Au film via the OPEs. The chip was removed, rinsed with acetone, and gently blown dry with  $\text{N}_2$ . The assembled NanoCells were electrically tested on a probe station with a semiconductor parameter analyzer at 297 K and  $10^{-5}$  mmHg, to give the typical current-vs-voltage ( $I(V)$ ) characteristics shown in **Figure 5**.<sup>36</sup>

Several mechanisms have been proposed for molecular electronic switching.<sup>65–67</sup> They are based on the idea that electrical charging of the molecules results in changes in the contiguous structure of the lowest unoccupied molecular orbital (LUMO). This can be accompanied by conformational changes that would modulate the current based on changes in the extended  $\pi$  overlap. As the voltage is increased, the molecules in discrete nanodomains would enter into different electronic states. Conversely, the so-called “molecular-based” switching may not be an inherently molecular phenomenon, but may result from surface bonding rearrangements that originate from the contact between the molecule and the metal (i.e., a sulfur atom changing its hybridization state or, more simply, sub-angstrom shifts between different gold surface-atom bonding modes, or molecular tilting).<sup>68</sup> In addition to a molecular electronic effect, electrode migration was considered next as a cause for the high currents and reset operations that are analogous to filamentary metal memories.<sup>69</sup> We carried out  $I(V,T)$  measurements (current as a function of voltage and temperature:  $-2$  to  $2$  V; 280 K to 80 K and back to 280 K) to assess the possible conduction mechanism of the high  $\sigma$  conductivity-type memory state on the bare chip. The data suggested “dirty” or modified-metal conduction: metallic conduction with trace impurities.<sup>70</sup>

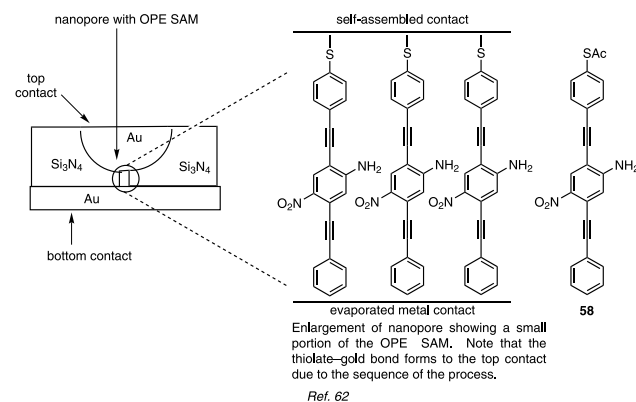
#### 2.4. The MolePore

We later developed a new test bed, the MolePore, for exploring the electrical properties of single molecules to eliminate the possibility of metal nanofilament formation and to ensure that molecular effects are measured (**Figure 6**).<sup>70</sup> This metal-free system used single-crystal silicon and single-walled carbon nanotubes as electrodes for the molecular monolayer and, as discussed earlier, the direct silicon–aryl carbon grafting protocol was utilized. The molecules being tested were grafted onto the hydride-passivated silicon substrate to form a monolayer in a small well made through the silicon oxide layer (Figure 6b). All molecules were directly bound to the Si surface via a Si–C bond; there was no intervening oxide. The area of the SWNT mat that was in contact with the metal pad (Figure 6c) was designed to be much larger than the area of the SWNT mat in contact with the molecular layer contained in the well. The SWNTs that were employed to bridge the grafted molecules included pristine SWNTs and SWNTs slightly functionalized with 4-tetradecylphenylene moieties. Both the pristine and functionalized SWNTs yielded similar electronic characteristics in the final devices.

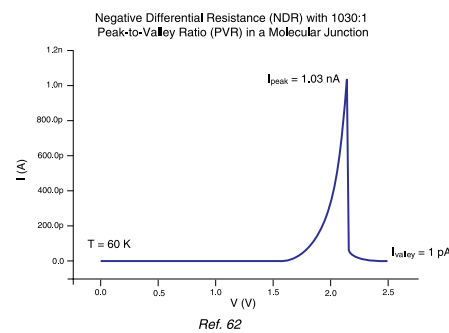
Use of this structure with  $\pi$ -conjugated organic molecules resulted in a hysteresis loop with  $I(V)$  measurements that are



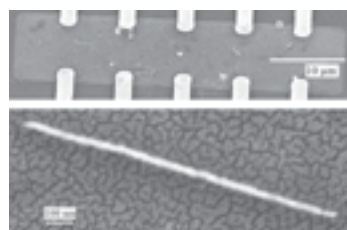
**Scheme 11.** Attachment of Single-Walled Carbon Nanotubes to a Silicon Surface Using Orthogonally Functionalized OPEs.



**Figure 2.** The Nanopore Test Bed Structure Containing a SAM of Functionalized OPE **58**.

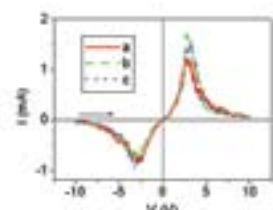


**Figure 3.** Current as a Function of Voltage [ $I(V)$ ] Characteristics of a Nanopore Test Bed Device Containing a SAM of Molecule **58** at 60 K. The Peak Current Density Is  $\sim 50$  A/cm<sup>2</sup>, and the Peak-to-Valley Ratio (PVR) of the Negative Differential Resistance (NDR) Response is 1030:1.



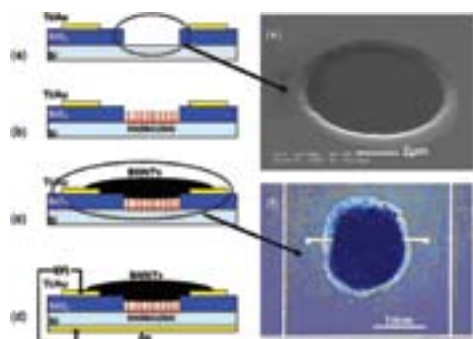
Ref. 36

**Figure 4.** SEM Image of the NanoCell after Assembly of the Au Nanowires and OPE **23**. The Top Image Shows the Five Juxtaposed Pairs of Fabricated Leads Across the NanoCell, and Some Au Nanowires Are Barely Visible on the Internal Rectangle of the Discontinuous Au Film. The Lower Image Is a Higher Magnification of the NanoCell's Central Portion Showing the Disordered Discontinuous Au Film with an Attached Au Nanowire, Which Is Affixed via the OPE-dithiol (Not Observable) Derived from **23**.



Ref. 36

**Figure 5.** Current vs Voltage [ $I(V)$ ] Characteristics of the NanoCell at 297 K. The Curves for a, b, and c Are the First, Second, and Third Sweeps, Respectively ( $\sim 40$  s/scan). The PVRs in c Are 23:1 and 32:1 for the Negative and Positive Switching Peaks, Respectively. The Black Arrow Indicates the Sweep Direction of Negative to Positive.



Ref. 70

**Figure 6.** A Schematic Is Shown of the Si-Molecule-SWNT Device and Its Fabrication Process: (a) the Starting Lithographically Defined Structure; (b) Formation of a Molecular Monolayer in the Well by Surface Grafting to Form a Direct Si-Aryl Carbon Bond; (c) Deposition of a SWNT Mat Atop the Molecules and Across the Well, Electrically Connecting the Molecular Layer to the Metal Pads; (d) the Finished Device after Bottom-Side Au Contact Formation; (e) an SEM Image of a 5- $\mu\text{m}$  Well Showing Its Ramped Oxide Edges; and (f) the Top View of a Finished Device Ready for Testing, Where the SWNTs Drape Across Both the Au Contacts and the Molecular Layer in the Well, the Latter Being a Minute Portion in the Center of the Image and Is Not Visible Due to the SWNT Mat and the Resolution of the Image.

useful for an electronic memory device. The memory is nonvolatile over  $>3$  days, nondestructive over  $>1,000$  reading operations, and capable of  $>1,000$  write-erase cycles before device breakdown. Temperature-independent  $I(V)$  behavior was observed. Devices without  $\pi$ -conjugated molecules (Si-H surface only) or with long-chain alkyl-bearing molecules produced no hysteresis, indicating that the observed memory effect is molecularly relevant.

### 3. Conclusion

Our synthetic efforts to make OTEs, OPEs, OPVs, and many other classes<sup>71</sup> of molecular electronics candidates has far outpaced our ability to have these molecules evaluated in relevant test beds.<sup>20</sup> Nevertheless, the availability of such a rich tool box of molecular architecture has led to discoveries not only in molecular electronics,<sup>1</sup> a few of which we have enumerated here, but also to advances in nanomachinery<sup>72</sup> and in educational outreach programs.<sup>73</sup> Research continues in our laboratory to further exploit our ability to graft molecular layers onto semiconductors and metals in order to build molecular electronics test beds and memory devices.

The work carried out in our laboratory is interdisciplinary in nature. Not only are we concerned with synthetic organic chemistry, but also materials, analytical, surface, and inorganic chemistries, as well as electrical engineering, materials engineering, and computer science. The need to work in all of these fields has brought many dedicated workers to our laboratories, and we thank them for their diligence in advancing the field. We look forward to many more fruitful and exciting collaborations with the hope that they will change the technology used in the world of tomorrow.

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